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UV Photolysis and Thermal Annealing of H_2S, HI, and H_2CO in Solid Xe: Electronic Absorption Spectra of the Products

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Photochemical studies on H_2S, HI, and H_2CO in solid Xe matrix are described with emphasis on the electronic absorption spectra of the products containing xenon atoms such as HXeSH, HXeI, and HXeH. These rare-gas molecules were prepared using UV photolysis of the precursors and annealing of the matrixes. The assignments are based on correlation between the UV spectra and known IR absorption bands of HXeSH, HXeI, and HXeH. It was found that the absorption maximum of HXeSH is near 290 nm, HXeI has two maxima at 310 and 410 nm, and HXeH absorbs around 230 nm. The present direct absorption measurements are in good agreement with previous photodecomposition data on HXeH.

Introduction

During the past several years, the rare-gas (Rg) compounds of a general type HRgY (Y is an electronegative fragment) have been subjected to a systematic series of investigations in low-temperature matrixes.[1] The synthesis of these unusual molecules is based on photodissociation of a suitable hydrogen-donating precursor HY followed by thermal activation of atomic hydrogen mobility. In the first series of experiments, HI, HBr, and HCl were used as precursors for the rare gas containing species.[2] It was found quite soon afterward that several polyatomic precursors such as H_2O, H_2S, HCN, and HNCO behave similarly,[1] and by now 13 HRgY molecules have been characterized in low-temperature matrixes, including an argon-containing molecule, HArF.[3] A peculiarity among these is the xenon dihydride molecule, HXeH for which a two-electron three-center binding model has been proposed.[4] Due to their strong H−Rg stretching absorption, HRgY's can be detected with relatively high sensitivity by infrared (IR) absorption spectroscopy.

Once formed, HRgY's are thermally stable at temperatures of a matrix-isolation experiment. However, they are efficiently destroyed when the matrix is irradiated in the UV or, in some cases, visible spectral range. For example, HXeI disappears in a few hundred of pulses from a 193 nm laser (~24 mJ/cm^2/pulse).[5] The observed photosensitivity of the HRgY molecules is evidently caused by strong charge-transfer absorptions onto a repulsive excited electronic state. The existence of such transitions was recently verified by direct absorption measurements in HCl-, HBr-, HI-, and HCN-doped solid xenon; moreover, their transition dipoles were predicted to exceed 7 Debye by multireference configuration interaction calculations.[5] As found in ref 5 and in our more recent report on HXeOH and HXeH,[6] the electronic absorption spectra of HRgY are broad and do not possess vibrational structure. Hence, spectral assignments have to be based on comparison between IR and UV data, preferably obtained from the same matrix. An alternative method for extracting the electronic absorption profiles relies on measuring the wavelength dependence of the photodecomposition efficiency of HRgY. Here, IR spectroscopy is used for monitoring and photolysis is carried out with tunable radiation. By assuming a constant quantum efficiency for dissociation, this method should yield profiles very similar to the actual absorption spectra. This method of extracting spectra has been successfully applied for HKrCl, HArF, HKrF, HXeOH, and HXeH.[6−8]

With respect to our understanding of chemical bonding in heavier rare gases, HXeH is perhaps the most interesting species. However, our previous attempts to extract its electronic spectrum in photolyzed H_2O-doped xenon suffered from interference due to overlapping absorption by HXeOH. In the present work we have selected H_2S, HI, and H_2CO as precursors for studies which aim at UV spectroscopic description of various photolysis and annealing products, including HXeSH and HXeH.

Experimental Section

The matrixes were deposited onto a MgF_2 substrate placed in a closed-cycle helium refrigerator (Displex DE-202A) at 45 K. The total amount of deposited gas was ~3 mmol. As a matrix film of sufficient thickness was grown, the sample was annealed at 50−55 K in order to minimize changes in the optical characteristics during the actual experiments. All spectral measurements were carried out at ~10 K. The temperature of the cold substrate was measured with a silicon diode and controlled with a LakeShore 330 controller unit. The dilution ratio between the precursor and Xe was typically 1:1000 to 1:500. H_2S of 99.8% purity and Xe of 99.997% purity were obtained from Messer Griesheim and AGA, respectively, and were used without further purification. HI was synthesized from iodine, red phosphorus, and water and purified by low-temperature distillation.[9] H_2CO was released from paraformaldehyde (Sigma).[10]

The UV spectra were recorded with an absorption spectrometer composed of a deuterium lamp (Cathodeon, V01), a 125 mm spectrograph (Oriel Instruments, MS125), and an image-intensified charge-coupled device (ICCD) detector (Andor

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Technologies). The wavelength scale of the detection system was calibrated with a Hg penlamp. The background spectra were measured through the samples prior to the photolysis. The IR absorption spectra were measured with a Nicolet Magna IR 760 spectrometer equipped with a KBr beam splitter and a HgCdTe detector. The MgF_2 substrate, essential for the UV measurements, limited the detection window in the IR to the range >1000 cm^{-1}. The samples were irradiated using a 193 nm excimer laser (Lambda Physik, Optex), a 248 nm excimer laser (Lambda Physics, Optex), a 308 nm excimer laser (Estonian Academy of Sciences, ELI-94), a xenon lamp (Oriel), or a deuterium lamp (Cathodeon, V01). Electronic excitations of the photolysis products was provided by the second-harmonic radiation of an optical parametric oscillator (OPO Sunlite with FX-1, Continuum), with pulse duration of 5−7 ns and pulse energy of ∼10 mJ. Photoluminescence was recorded with a UV−visible spectrograph (Spex 270M, resolution 0.3 nm) equipped with a gated ICCD camera (Princeton Instruments).

Results and Discussion

H_2S/Xe Matrix. IR absorption spectra of our H_2S/Xe matrixes were quite similar to what is previously reported for H_2S doped Xe crystals[11] and Xe matrixes.[12] Upon 193 nm photolysis of the matrix, more than 90% of the total amount of H_2S, including monomers and multimers, was dissociated. Parallel to the decrease of the H_2S lines, formation of a photolysis product was indicated by a new line at 2550.5 cm^{-1}. On the basis of the previous studies, this absorption belongs to the $SH\cdots H_2S$ complex.[12] Annealing of the extensively photolyzed sample at 48 K induced new absorption bands at 1112, 1119, 1136, 1166, and 1181 cm^{-1} due to formation of HXeSH (first three) and HXeH (last two).[4,13] An additional photolysis at a longer wavelength, 308 nm, bleached the HXeSH absorption bands completely; however, HXeH was not affected by irradiation at this wavelength, in agreement with our recent data on UV decomposition of HXeH.[6] Further photolysis at 193 nm caused complete disappearance of the HXeH lines at 1166 and 1181 cm^{-1}.

Upon 193 nm photolysis of matrix isolated H_2S, the most prominent new spectral features in the UV absorption spectrum were the relatively sharp peaks at 199, 234, 242, 319, and 337 nm and a resolved vibronic band between 265 and 314 nm (Figure 1a). The peak at 199 nm and the progression on its blue side can be assigned to the xenon caged hydrogen atom[14] and the vibronic progression to the $B\ ^3\Sigma^-_u \leftarrow X\ ^3\Sigma^-_g\ (v'' = 0)$ system of S_2 trapped in a Xe matrix.[15]

We assign the 337 and 319 nm absorptions to the SH radical in solid Xe. The measurements showed that the 337 and 319 nm absorptions seen in Figure 1a belong to the same absorber moreover, they closely resemble the vibrational pattern observed in the excitation spectrum of the SH radical emission at 426 nm (see Figure. 2). The gas-phase values for the (0,0) and (1,0) vibronic lines of the $A\ ^2\Sigma^+ \leftarrow X\ ^2\Pi$ transition of the SH radical are at 323.7 and 306.1 nm, respectively.[16] In an argon matrix, the transitions are red shifted to 328.9 and 310 nm, respectively.[17] Koda et al. have recently reported a very similar spectrum for SH radical isolated in a free-standing krypton crystal.[18] The strong bands at 234 and 242 nm, which unambiguously belong to some photolysis product but do not seem to have counterparts in the IR absorption spectra, are most likely due to XeS charge transfer. This assignment can be readily substantiated by the recent work on the charge transfer states of RgS by Gudipati and Klein.[19] The empiricaly derived ionic potentials of ref 19 predict an excitation energy of ∼6.5 eV for a XeS pair with an internuclear distance of ∼4 Å corresponding to the approximate separation of Xe and S in a substitutional site of a Xe lattice. In Xe surroundings the charge transfer states are stabilized by ∼1.2 eV,[19] resulting in an excitation energy of ∼5.3 eV, or 234 nm. This is, in fact, in excellent agreement with the present results. More support for the assignment that XeS is responsible for the observed absorptions at 234 and 242 nm is provided by the result by Tanaka et al. that XeS charge transfer state can be excited at 248 nm.[20]

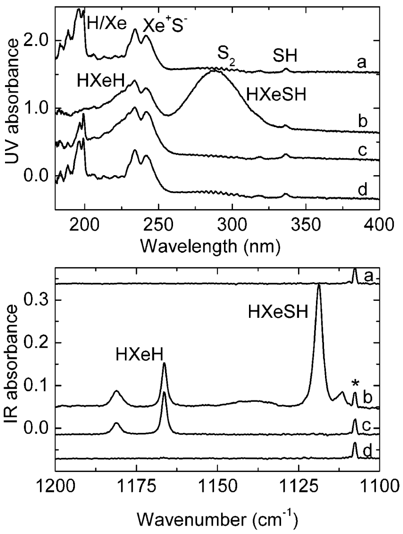

Figure 1. IR (lower panel) and UV (upper panel) absorption spectra of a H_2S/Xe matrix: (a) after approximately 90% of H_2S was photolyzed with a 193 nm laser, (b) after annealing the photolyzed matrix at 48 K, (c) second photolysis at 308 nm with 100 pulses, and (d) third photolysis at 193 nm with 630 pulses. The known absorbers are indicated. The broad absorption centered at 290 nm is assigned to the HXeSH molecule. Impurity IR absorption peak is marked with an asterisk.

The photolyzed H_2S/Xe sample was annealed at 48 K when the maximum in the SH radical concentration was reached in the photolysis. As seen in Figure 1b and Figure 6b, a very strong broad UV absorption grew near 290 nm upon annealing. Additionally, another thermally induced broad absorption was observed near 230 nm. Simultaneous with the appearance of these bands, the SH radical absorption decreased by ca. 60%, the absorption of the xenon caged hydrogen disappeared completely, and the XeS absorptions were partially diminished.

The absorption bands at 290 and 230 nm can be efficiently bleached by UV photons, but they bleach at different wavelengths. Irradiation at 308 nm caused the band at 290 nm to disappear, while the 230 nm absorption was unchanged. The decrease of the 290 nm band correlated with simultaneous increase of the absorptions due to the SH radical and xenon caged hydrogen atom. Additional irradiation at 193 nm bleached the 230 nm absorption completely and caused a further ∼25% increase of hydrogen absorption. By comparing the changes in UV absorption intensities, it can be estimated that ca. 40% of the initially photogenerated hydrogen atoms are permanently lost in thermal reactions during the first annealing period. The second annealing at 48 K after the two photolysis steps at 308 and 193 nm yielded ca. 30% and 60% less intensity at 290 and 230 nm, respectively, compared with the first annealing. Interestingly, further irradiation at 308 and 193 nm recovered 95% of hydrogen atoms with respect to their concentration after the first annealing−photolysis cycle. The surprisingly high recovery of hydrogen atoms might be caused by the partial photodissociation of SH radical content during the photobleaching of 230 nm absorption at 193 nm. The photolysis-annealing

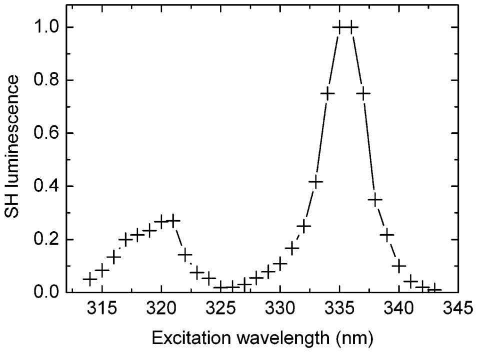

Figure 2. Excitation spectrum of the SH radical emission recorded at 426 nm. See ref 21 for the experimental details.

behavior of the IR absorption spectra of HXeSH and HXeH are correlated with the UV absorption spectra of the same sample in Figure 1. These data are sufficient to assign the UV absorption band at 290 nm to HXeSH. Furthermore, the 230 nm band likely originates from HXeH, in agreement with the discussion of ref 6, although the correlation of this band with the HXeH concentration is less clear due to modifications of the bands at 234 and 242 nm. This assignment is confirmed later.

At the early stage of photolysis of H_2S in a Xe matrix, the xenon-caged hydrogen atom and the XeS band at 242 nm were the most prominent absorptions. Further irradiation produced the absorption bands due to SH and S_2 and a the XeS band at 234 nm. Finally, prolonged irradiation of the matrix at 193 nm caused total disappearance of the SH bands and significant increase of the H/Xe, S_2, and 234 nm absorptions. The increase of the S_2 absorption is probably due to photolysis of H_2S dimers and possibly due to photoinduced mobility of S atoms released in the photodissociation of SH radicals.[21]

HI/Xe Matrix. The IR, UV, and visible absorption spectra of a HI/Xe sample and its photolysis and annealing products were reinvestigated in order to confirm the shape of the absorption band of HXeH and, also, to detect a possible visible absorption of the HXeI molecule.[22] A HI/Xe sample (~1:1000) shows the most prominent absorptions at 2145, 2166, and 2215 cm^{-1}. The 2215 cm^{-1} band and the broad feature on its red side both belong to the HI monomer, while the 2166 and 2145 cm^{-1} absorptions are assigned to the dimer and trimer, respectively.[23] It was also suggested that the 2145 cm^{-1} peak could belong to the H_2O-HI complex.[24]

Photolysis at 193 nm caused complete disappearance of the HI absorptions after 4000 laser pulses ($\sim 2.3 \times 10^{16}$ photons/cm^2/pulse). After the photolyzed sample was annealed at 48 K, the IR spectrum indicated formation of HXeI and HXeH. The absorptions of HXeI at 1187, 1193, and 1215 cm^{-1} were very efficiently photobleached by 308 nm radiation ($\sim 8 \times 10^{15}$ photons/cm^2/pulse) or using a filtered Xe lamp with spectral range $\geq$ 400 nm. Irradiation with these light sources caused only minor changes in the absorptions of HXeH at 1166 and 1181 cm^{-1}. The main new features in the UV absorption spectrum after photolysis of the HI/Xe matrixes were the well-structured charge-transfer absorption bands of Xe^+I^- system between ca. 210−290 nm and the H/Xe charge-transfer absorption at 199 nm (Figure 3).[25,14] It should be noted that the weak intensity of the H/Xe absorption is most probably due to poor transmission of this particular sample near 200 nm rather than due to low concentration of hydrogen atoms produced in the photolysis.

Upon annealing of the photolyzed sample at 48 K, two broad absorption bands grew at 230 and 310 nm (Figures 3b and 6a). The latter absorption has been previously assigned to HXeI.[5]

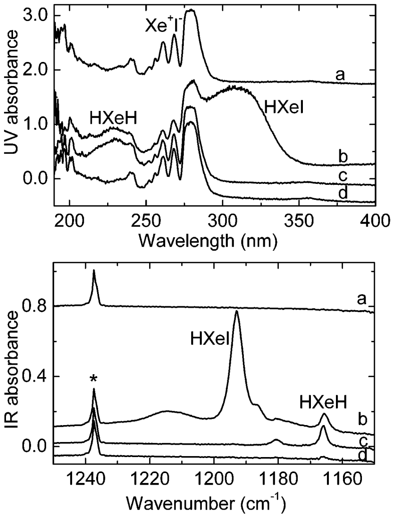

Figure 3. IR (lower panel) and UV (upper panel) absorption spectra of a HI/Xe matrix: (a) after 193 nm photolysis of HI/Xe sample, (b) annealing at 48 K, (c) second photolysis at 308 nm with 50 pulses, and (d) third photolysis at 193 nm with 500 pulses. Impurity IR absorption peak is marked with an asterisk.

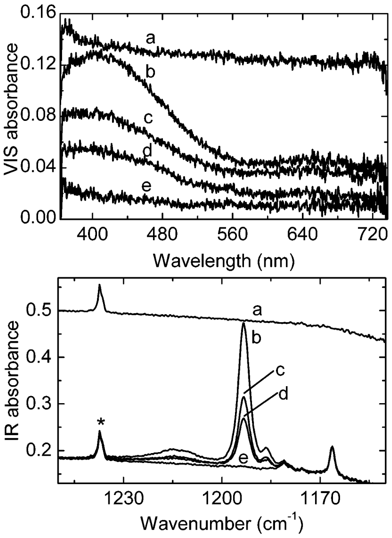

Figure 4. Correspondence between IR and visible absorptions of HXeI: (a) after 193 nm photolysis of a HI/Xe matrix, (b) after annealing at 48 K, and (c−e) after Xe-lamp photolysis with a cutoff filter ($\geq$400 nm) for 60, 80, and 620 s, respectively. Impurity peak is marked with an asterisk.

The correlation of the IR and UV absorptions is presented in Figure 3. The 230 nm band bleaches upon 193 nm irradiation, correlating with the decrease of the HXeH concentration, which confirms the assignment of this UV absorption to HXeH.

A new absorption was observed in the visible spectral range near 410 nm when the sample was annealed at 48 K (Figure 4). This absorption was efficiently photobleached with a filtered Xe lamp ($\lambda \geq 400$ nm). The close similarity of the behavior of this 410 nm absorption and the IR absorption spectrum of HXeI (see Figure 4c−e) strongly suggests that this absorption band belongs to the HXeI molecule too. The observation of this absorption is consistent with the efficient decomposition of HXeI at visible wavelengths.[22, 24]

It should be noticed that annealing of the photolyzed HI/Xe matrixes leads to an essential decrease of the electronegative participant (I atoms). Moreover, the photodecomposition of HXeI molecules recovers a large part of I atoms. These data are in good agreement with the IR absorption results of ref 22

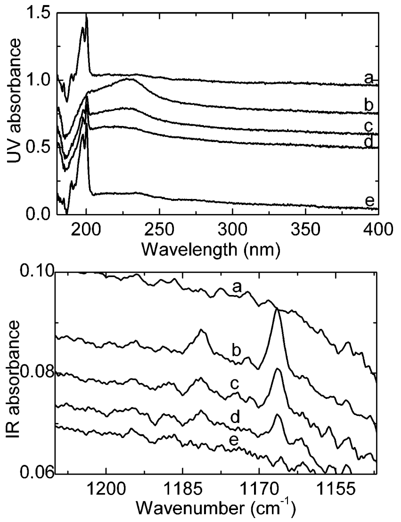

Figure 5. IR (lower panel) and UV (lower panel) absorption spectra of H_2CO/Xe matrix: (a) after 248 nm photolysis, (b) after annealing at 48 K, and (c−e) second photolysis at 193 nm with 10, 20, and thousands of pulses, respectively.

and demonstrate rather small permanent losses of H atoms at stages of photolysis and annealing. The most important channel of permanent losses is believed to be formation of H_2 molecules. The qualitative agreement with the present experiments on H_2S/Xe matrixes is remarkable here, and further discussions can be found elsewhere.[1]

H_2CO/Xe Matrix. The infrared absorption spectrum of H_2CO in solid Xe consists of structured peaks in the 1480−1510, 1700−1740, and 2680−3000 cm^{-1} spectral regions. These absorptions most probably arise from formaldehyde monomer, dimer, and higher polymers in accordance with the results in nitrogen and argon matrixes.[26,27] More detailed studies of H_2CO in rare gas matrixes are in progress in our laboratory;[28] therefore, we do not provide detailed spectral assignments here.

H_2CO possesses two distinct dissociation channels in the gas phase, namely, $H_2CO \rightarrow H + HCO$ and $H_2CO \rightarrow H_2 + CO$.[29] Among these, the first reaction would provide a convenient precursor for H atoms for the present investigations of HXeH. After extensive UV irradiation with a KrF laser at 248 nm ($\sim 5 \times 10^{20}$ photons/cm^2/pulse), more than 90% of the formaldehyde was dissociated, and simultaneous growth of the CO absorption was observed. Although not detected by IR spectroscopy, the existence of HCO intermediate was verified by Electron Paramagentic Resonance (EPR).[28] Subsequent annealing of the photolyzed sample at 48 K caused appearance of the absorptions of HXeH at 1166 and 1181 cm^{-1} and the absorption of HCO at 1858 cm^{-1}.[24,30] The absorptions of HXeH were completely photobleached after 50 laser pulses at 193 nm, while there was only minor change in the HCO absorption.

A UV spectrum of the photolyzed H_2CO sample showed only the absorption due to the xenon caged hydrogen atom near 200 nm (see Figure 5). [14] The negative signal, which indicates here photodissociation of the absorber, on the blue side of the hydrogen absorption most probably belongs to the first Rydberg absorption of H_2CO.[31] During annealing of the photolyzed sample at 48 K, a broad absorption appeared at 230 nm and the absorption of xenon caged hydrogen completely disappeared (Figure 5b and 6c). Subsequent photolysis at 193 nm destroyed this absorber very effectively, as seen in Figure 5. Although the IR absorption of HXeH is weak, the correlation between IR and UV measurements makes us finally confident that the 230 nm band belongs to HXeH.

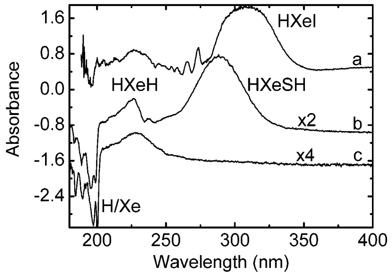

Figure 6. UV difference spectra between (a) panels a and b of Figure 3, (b) panels a and b of Figure 1, and (c) panels a and b of Figure 5. Positive and negative signals show absorptions which increase or decrease, respectively.

The 230 nm band assigned to HXeH agree well with the HXeH photodecomposition profile reported by us previously.[6] This agreement confirms that the decomposition spectroscopy method provides reliable data on electronic absorption spectra of HRgY molecules.[6−8]

Conclusions

We investigated electronic absorption spectra of products obtained in UV photolysis and annealing experiments with H_2S, HI, and H_2CO in solid Xe. As the main goal, the UV absorption of HXeH in reliably identified to be at 230 nm. Unfortunately, the excited states of this molecule have not been characterized; thus, the nature of this transition cannot be deduced with confidence. However, the strength of this absorption would strongly suggest charge transfer for its origin. The question concerning the role of the Xe environment in the 230 nm absorption must be left for future investigations. The broad UV absorption bands of HXeSH is at 290 nm. In addition to the previously reported band near 310 nm, HXeI has an absorption band at 410 nm. The present data show the agreement between photodecomposition profiles of HXeH and its UV absorption spectrum, justifying photodecomposition spectroscopy as a reliable and selective tool to study electronic absorption spectra of HRgY molecules. It is shown that the formation of rare-gas molecules consumes the main part of photoproduced H atoms. In agreement with the previous studies,[1] we supported here the minor permanent losses of H atoms at stages of UV photolysis of small hydrogen-containing molecules (H_2S, HI, etc.) and posterior annealing.

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